Rydberg states of polyatomic molecules using model potentials

Timothy C. Betts* and Vincent McKoy

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91109
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We have used a simple model potential to calculate the Rydberg series in carbon dioxide, nitrogen dioxide, nitrous oxide, acetylene, propyne, formaldehyde, allene, butadiene, and butene. The model potential for a molecule is taken as a sum of atomic model potentials. The results agree well with experiment and allow us to assign and interpret almost all the Rydberg series in the molecules studied. In addition to various applications we can identify several Rydberg series which are perturbed by interloping valence transitions, e.g., in H_2CO and CO_2.

I. INTRODUCTION

In an earlier paper[1] we developed a method of determining Rydberg states of polyatomic molecules using a molecular model potential which was taken as a sum of atomic model potentials calibrated to atomic data and containing no further parameters. This method was applied to the molecules nitrogen, oxygen, carbon monoxide, nitric oxide, ethylene, and benzene and gave results accurate to within 5%–10% in all cases.

In this paper we apply the same method to another group of molecules for which the experimental spectra are readily available but have not been completely assigned. The basis of the method has been thoroughly discussed in the first paper and hence this paper will differ somewhat in that emphasis will be placed on the interpretation of the spectra using the results of our calculations while the calculations themselves will be discussed only briefly. Next we give a brief summary of the method and its implementation.

The pseudopotential method is based on the transformation of the standard wave equation for a valence electron,[2]

$$(T+V)\psi_v = E_v\psi_v, \tag{1}$$

into the new equation,

$$(H+V_p)\phi_v = (T+V+V_p)\phi_v = E_v\phi_v, \tag{2}$$

where V_p is a nonlocal repulsive pseudopotential which cancels off most of V, leaving a weak effective potential $V+V_p$. In Eq. (2) ϕ_v is a pseudowavefunction which is equal to ψ_v outside the molecular core, but inside the core has the oscillations of ψ_v removed. Since V_p is defined by the equation,

$$V_p\phi = \sum_c \langle F_c|\phi\rangle\psi_c, \tag{3}$$

where F_c are arbitrary functions and the ψ_c are solutions of

$$(T+V)\psi_c = E_c\psi_c \tag{4}$$

representing "core" states, V_p is not unique. In fact, the ϕ_v are not unique either and there are several possible choices for V_p and ϕ_v. The model potential method takes advantage of this latitude in assuming that there exists a V_p which can be approximated by a simple function V_m which yields suitable wavefunctions ϕ_v. For atoms, Abarenkov and Heine[3] suggested a model potential of the form

$$\begin{aligned} V_M &= A, && r < r_0 \\ &= \delta Z/r, && r \geq r_0, \end{aligned} \tag{5}$$

where A is a constant, r_0 represents the radius of the atomic core, and δZ the effective charge on the atomic core. For molecules this choice for model potentials can be extended to

$$V_{\text{molecule}} = \sum_{\text{atoms}} V_{\text{atom}} \ . \tag{6}$$

This has the advantage of fixing all the molecular parameters by calibration to atomic data.

To use these equations we must determine the various parameters. To determine the A's for the atoms we set $\delta Z = 1$ and $r_0 = 2.5$ a.u. and solve the resulting atomic Rydberg equations for various values of A until the calculated spectrum agrees with the experimental term values for that atom. In this paper we have used the values of 0.375, 0.115, and 0.045 a.u. for carbon, nitrogen, and oxygen, respectively. To determine the δZ's we can frequently make use of symmetry. δZ for an atom is obviously equal to one. For homonuclear and heteronuclear diatomic molecules we choose $\delta Z = \frac{1}{2}$. In general, we use $\delta Z = 1/n$ for a molecule containing n atoms. This is not always the best procedure and we can get results in better agreement with experiment in some cases by varying δZ. This introduces a new parameter into the molecular calibration. As another simplifying assumption we neglect the effect of the hydrogen atoms. This assumption has been tested[1] and leads to no significant differences in the calculated spectra. With these calibrations and assumptions the resulting equations are set up in a basis of Gaussian functions and solved by standard matrix techniques. The actual calculations are very rapid.

The results of these calculations are sufficiently accurate to be applicable to the problems of molecular spectroscopy. There were only a few transitions in the molecules we have studied which could not be definitely assigned using the results of these model calculations. Among the interesting problems discussed in this paper are the confirmation of the lowest ionization limit in nitrogen dioxide, the re-establishment of Duncan's Rydberg series in nitrous oxide, and an explanation of the so-called "mystery bands" in *trans*- and *cis*-butene. These problems along with others discussed in this paper and Ref. 1, are typical of the uses to which model potential calculations of Rydberg states can be put.

TABLE I. Rydberg series in CO_2.[a]

Rydberg orbital	Calculated term values[b]	Experimental term values	
$3s\sigma_g$	3.39[c]	...	
$4s$	1.50	1.56[d]	
$5s$	0.84	0.83	
$6s$	0.52	0.54	
$3p\sigma_u$	2.47	2.40[e]	...
$4p$	1.19	1.15	1.12[f]
$5p$	0.70	0.68	0.71
$6p$	0.45	0.45	0.48
$3p\pi_u$	2.37	2.81[g]	...
$4p$	1.11	1.32	1.12[h]
$3d\pi$	1.91	1.90[i]	
$4d\pi$	0.94	1.00	

[a]Ground state configuration, $1\sigma_u^2 1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4 - {}^1\Sigma_g^+$.
[b]All term values in electron volts.
[c]Quantum defect $\delta = 1.0$.
[d]Averages of the term values for the $1\pi_g^2 ns\sigma_g$, $1\pi_u^3 ns\sigma_g$, and $3\sigma_u 3\sigma_u ns\sigma_g$ series.
[e]Term values for the $1\pi_g^3 np\sigma_u$ series. See Ref. 5.
[f]Term values for the $4\sigma_g np\sigma_u$ series.
[g]Term values for the $1\pi_g^3 np\pi_u$ series. See Ref. 5.
[h]Term value for the $4\sigma_g np\pi_u$ series.
[i]Quantum defect $\delta = 0.32$. Term values are those of Henning's diffuse series.

II. RESULTS

A. Carbon dioxide

The Rydberg series in carbon dioxide have been extensively studied. Series have been observed converging to four different ions at 13.8, 17.3, 18.1, and 19.4 eV, respectively. Herzberg[4] has identified the lowest of these ions with the $^2\Pi_g$ states of CO_2^+. Rydberg states appear in the optical spectrum below 1150 Å. Four Rydberg series, two strong and two weak, converge to the first ionization limit. The strong series have quantum defects of 0.65 while the weak series have quantum defects of 0.97 and 0.57. Two series, with quantum defects given by the expressions $\delta = n - 0.063 - 0.0069/n$ and $\delta = n - 0.04 - 0.34/n$ converge to the second ion. Two more series, known as Henning's sharp and diffuse series, with quantum defects of 0.01 and 0.34, respectively, converge to the third ion. Finally series with quantum defects of 0.71, 0.56, and 0.05 converge to the ion at 19.4 eV.[5]

From the results of our calculations in Table I we can assign most of the observed series. Henning's sharp series with observed term values[5] of 1.60, 0.80, and 0.54 has to be assigned as the $ns\sigma_g$ series while we have assigned Henning's diffuse series as $nd\pi_g$. The calculated term values of 1.91 and 0.94 eV agree very well with the observed values of 1.90 and 1.0 eV, respectively. This assignment is in better agreement with experiment than the other suggested assignment[6] of the diffuse series as $nd\sigma_g$ with its calculated term values of 2.27 and 0.92 eV and a quantum defect of 0.55. We have also assigned the Rydberg series with members at 10.98, 12.47, and 13.03 eV (term values of 2.81, 1.32, and 0.76 eV, respectively) as an $np\pi_u$ series and the states at 11.39, 12.64, and 13.11 eV (term values of 2.40, 1.15, and 0.68 eV) as an $np\sigma_u$ Rydberg series. Both of these Rydberg series are superimposed on a strong continuumlike absorption which is probably predominantly due to excitation of the valencelike $^1\Sigma_u^+ (1\pi_g \rightarrow \pi_u)$ state.[7] The $^1\Sigma_u^+$ Rydberg states, i.e., the $np\pi_u$ series can be expected to be more strongly perturbed by this underlying continuum leading to a lowering of the hypothetical unperturbed $np\sigma_u$ levels and hence the larger term values. The observed quantum defects for this np series are larger than typical defects of np series.[1,8] Also recent calculations which allow for the perturbation of the $^1\Sigma_u^+(1\pi_g \rightarrow 3p\pi_u)$ Rydberg state by a valencelike $^1\Sigma_u^+$ state put the $3p\pi_u$ state below the $3p\sigma_u$.[9]

B. Nitrogen dioxide

The ground state of NO_2 is bent while the NO_2^+ ions are linear. Hence transitions to higher Rydberg states must have an extended structure and are therefore not readily identified without a detailed analysis. This makes the identification of the Rydberg series in NO_2 more difficult than in the other molecules we have studied.

The only complete Rydberg series observed for nitrogen dioxide converges to an ion 18.9 eV above the ground state. Other series lead to estimates of lower lying ions at 9.8, 11.6, and 12.3 eV. From an analysis of the 1350–1650 Å region Ritchie and Walsh[10] concluded that the Rydberg states were of $^2\Sigma_u^+$ symmetry, i.e., a $np\sigma_u$ series. Price and Simpson[11] observed two short progressions which they assigned as a Rydberg series with a quantum defect of 0.75. Tanaka and Jursa[12] observed a series with quantum defect 0.65 and a limit at 12.1 eV. Series with quantum defects of 0.15, 1.03, and 0.67 all converge to the ion at 18.9 eV.

From our model calculations we can account for all these series. Table II shows our assignments. Of particular interest is the $\tilde{E}\,^2\Sigma_u^+$ state which we assign as the $n = 3$ member of the $np\sigma_u$ series. Its calculated term value is 2.50 and since it lies at 7.23 eV we can predict the first ionization limit to be approximately 9.73 eV. This agrees well with the value of 9.78 eV obtained from photoionization measurements.[13] The series with predicted limits at 11.6, 12.1, and 12.5 eV can be assigned as $^2\Sigma_u^+$ or $^2\Pi_u$ series with an $np\sigma_u$ or $np\pi_u$ orbital, respectively. However, we cannot pin down these two assignments any closer.

C. Nitrous oxide

For nitrous oxide Rydberg series are observed converging to ions at 12.9, 16.4, and 20.1 eV.[4] The first Rydberg state in the optical spectrum is a single sharp peak, the $\tilde{D}$ state, at 1292 Å near the maximum of a broad $\tilde{X} \rightarrow \tilde{C}$ absorption. Beyond this region two Rydberg series with quantum defects of 0.60 and 0.68, designated as series I and II, respectively, converge to the lowest state of NO_2^+. Two more Rydberg series with quantum defects of 1.0 (III) and 0.22 (IV) converge to the next ion at 16.4 eV. Finally four series, VI to IX, with

TABLE II. Rydberg series in NO_2.[a]

Rydberg orbital	Calculated term values[b]	Experimental term values
$3s\sigma_g$	3.09[c]	3.28[d]
$4s$	1.57	1.54
$5s$	0.87	0.88
$3p\sigma_u$	2.50[e]	2.55[f]
$4p$	1.20	1.24[g]
$5p$	0.71	0.74
$6p$	0.45	0.48
$3d\sigma$	1.75[h]	1.66[i]
$4d$	0.93	0.90

[a]Electron configuration of linear NO_2 $1\sigma_u^2 1\sigma_g^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 1\pi_u^2 3\sigma_u^2 1\pi^4 5\sigma_g - {}^2\Sigma_g^+$.
[b]All term values in electron volts.
[c]Quantum defect of 1.05.
[d]$^2\Sigma_g^+$ doublet series with limits at 152 160 and 152 390 cm^{-1}.
[e]Quantum defect of 0.65.
[f]$\tilde{E}\ ^2\Sigma_u^+$ state at 7.23 eV.
[g]$^2\Sigma_u^+$ or $^2\Pi_u$ series with a limit of 152 290 cm^{-1}.
[h]Quantum defect of 0.21.
[i]$^2\Sigma_g^+$ series.

quantum defects of 0.31, 0.06, 0.68, and 0.58, respectively, converge to the ion at 20.1 eV.[14] Rydberg series have also been seen in the electron impact spectra.[15]

From our model calculations we can consistently assign all the observed series. Table III gives these assignments. Experimental term values for the $ns\sigma$ series leading both to the $^2\Pi$ and $^2\Sigma$ ions at 12.90 and 16.40 eV, respectively, are shown in Table III. The difference between the term values for the $n=3$ member of the $^2\Pi$ and $^2\Sigma$ series, i.e., 3.40 and 4.03 eV, may indicate a perturbation of the $^2\Sigma(3s\sigma)$ state by some other state. From recent electron impact data[15] we can confirm Duncan's series as an $ns\sigma$ progression.[16] The series observed by Cook[14] can also be identified as an np progression. We can also assign the observed series VII with term values of 1.53, 0.83, and 0.52 and a qunatum defect of 1.06 as the 4s, 5s, and 6s members of the $ns\sigma$ series. This series was assigned as an $nd\pi$ series by Lindholm.[17] Similarly, we can now assign the series with term values of 1.56 and 0.87 eV, previously assigned as $nd\pi$,[17] as an $ns\sigma$ series. We also identify the series IV and VI as $nd\pi$ series and not as a $nd\sigma$ series[17] since the $n=3$ member of the $nd\sigma$ series is calculated to have a term value of 2.8 eV.

TABLE III. Rydberg series in N_2O.[a]

Rydberg orbital	Calculated term values	Experimental term values
$3s\sigma$	3.55[b]	3.40[c] 4.03[d]
$4s$	1.58	1.52 1.56
$5s$	0.87	0.85 0.86
$6s$	0.53	0.52
$3p\sigma$	2.46[e]	2.40[f]
$4p$	1.19	1.16
$5p$	0.70	0.71
$6p$	0.45	0.49
$3p\pi$	2.54[g]	2.56[h]
$4p$	1.24	1.24
$5p$	0.75	0.73
$6p$	0.47	0.49
$3d\pi$	1.58[i]	1.80[j]
$4d$	1.06	0.98
$5d$	0.65	0.61

[a]Ground state electron configuration, $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 7\sigma^2 2\pi^4 - {}^1\Sigma_g^+$.
[b]$\delta = 1.04$.
[c]From the electron impact spectrum of Ref. 15.
[d]Series III of Ref. 14.
[e]$\delta = 0.65$.
[f]Series II and IX of Ref. 14.
[g]$\delta = 0.68$.
[h]Series VIII of Ref. 14.
[i]$\delta = 0.24$.
[j]Average of Rydberg series IV and VI. See Ref. 14.

D. Acetylene and propyne

Two Rydberg series with quantum defects of 0.95 and 0.50 converge to the first ionization limit of acetylene at 11.4 eV.[4] From a high resolution analysis of the second member of the series with a quantum defect of 0.95, Herzberg[18] has shown that the state is of $^1\Pi_u$ symmetry. Moreover Wilkinson[19] has also shown that the nR' series with δ of about 0.50 is probably a Π_u series. Hence both of these series have upper states of Π_u symmetry. Table IV shows our assignments. The observed series with quantum defects of 0.95 and 0.50 are assigned as $ns\sigma$ and $nd\sigma$ series with calculated quantum defects of 0.99 and 0.59, respectively. The agreement with experiment is good. Table IV also includes the results of more detailed calculations for the $ns\sigma$ series by Duncan.[20]

Propyne has an optical spectrum similar to that of acetylene. Three series with quantum defects of 0.98, 0.57, and 0.33 are observed to converge to the lowest ion at 10.4 eV.[4] By comparison with the Rydberg series in acetylene, the first two series in propyne can be assigned as ns and nd series. The agreement with the experimental values listed in Table V is good. The term

TABLE IV. Rydberg series for acetylene.[a]

Rydberg orbital	Calculated term values		Experimental term values
$3s\sigma_g$	3.44[b]	...	3.24[d]
$4s$	1.50	1.46[c]	1.47
$5s$	0.84	0.80	0.83
$6s$	0.51	0.52	0.54
$3d\sigma_g$	2.35[e]		2.18[f]
$4d$	1.15		1.11
$5d$	0.71		0.67
$6d$	0.47		0.45

[a]Ground state electronic configuration: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 - {}^1\Sigma_g^+$.
[b]$\delta = 0.99$.
[c]Reference 20.
[d]Reference 18.
[e]$\delta = 0.59$.
[f]The nR' series of Ref. 19.

TABLE V. Rydberg series for propyne.

Rydberg orbital	Calculated term values[a]	Experimental term values
$3s$	3.10[b]	3.25[c]
$4s$	1.42	1.50[d]
$5s$	0.82	0.84
$6s$	0.52	0.54
$3d\sigma$	2.26[e]	2.25[f]
$4d$	1.18	1.13
$5d$	0.69	0.69

[a]In electron volts.
[b]$\delta = 0.90$.
[c]$\tilde{C}\ ^1E$ state, see Ref. 21.
[d]Average of ns series converging to ions at 10.4 and 11.29 eV.
[e]$\delta = 0.54$.
[f]nR' series of Ref. 22.

value for the $n = 3$ member of the ns series is from the series converging to the ion at 11.29 eV.[21] The $n = 3$ state of the ns series converging to the ion at 10.4 eV is not observed and is probably buried in the B continuum.[4] Our results do not give any states which could be reasonably assigned as the nR'' series with a quantum defect of 0.33.[22] Possible assignments are as a $nd\pi$ or $nd\sigma$ series.

E. Formaldehyde

Four Rydberg series with quatum defects of 1.04, 0.70, 0.70, and 0.4 converge to the lowest ion of formaldehyde at 10.9 eV.[4,23] Our assignments are shown in Table VI. The series with a quantum defect of 1.04 is clearly an ns series while the two series with quantum defects of 0.70 are npa_1 and npb_2 series. The observed term value for the $n = 3$ member of the npb_2 series is larger than the calculated term value, i.e., 2.91 eV compared to 2.59 eV. This is probably due to a perturbation of the $^1A_1(2b_2npb_2)$ Rydberg state by the valence $^1A_1(\pi \rightarrow \pi^*)$ state.[8] We have assigned the series with a quantum defect of 0.40 as an nd series. The model calculations support this large a quantum defect for an nd series.[4]

TABLE VI. Rydberg series for formaldehyde.[a]

Rydberg orbital	Calculated term values	Experimental term values
$3sa_1$	3.67[b]	3.80[c]
$4s$	1.57	1.63
$5s$	0.86	0.87
$6s$	0.52	0.55
$3pa_1$	2.64[d]	2.74[e]
$4p$	1.32	1.25
$5p$	0.77	0.74
$6p$	0.48	0.48
$3pb_2$	2.59[f]	2.91[g]
$4p$	1.25	1.29
$5p$	0.77	0.74
$6p$	0.47	0.48
$3d$	2.25[h]	2.01
$4d$	1.17	1.04
$5d$	0.71	0.63

[a]Ground state electron configuration $1a_1^2 2a_1^2 3a_1^2 4a_1^2 1b_2^2 5a_1^2 1b_1^2 2b_2^2 - {}^1A_1$.
[b]$\delta = 1.08$.
[c]$B\ ^1B_2$ state.
[d]$\delta = 0.73$.
[e]$\tilde{D}\ ^1B_2$ state.
[f]$\delta = 0.71$.
[g]$\tilde{C}\ ^1A_1$ state. This state is perturbed by another state of the same symmetry. See text.
[h]$\delta = 0.57$.

F. Allene

Below 1500 Å, Sutcliffe and Walsh[24] observed a large number of strong bands which they arranged into nine Rydberg series. Some of these series are fragmentary and must be vibrational members of the main Rydberg series. Six main Rydberg series, I–VI, with quantum defects of 1.06, 0.70, 0.55, 0.55, 0.40, and 0.30, respectively, converge to the lowest ion at 10.2 eV. Table VII shows our assignments. Series I with a quantum defect 1.06 is clearly an nsa_1. There can only be one such series and hence the other two series with quantum defects of about one reported by Sutcliffe and Walsh[24] must be vibrational members of series I. Series II–IV must be npb_2 and npe series. Series II is assigned as the npb_2 series, and the progressions III and IV are probably members of the npe series. The other series reported with a quantum defect of about 0.75 can be identified as a vibrational member of the series II. Finally, both series V and VI with quantum defects of 0.40 and 0.30, respectively, can be assigned as nd series. Hence we can account for all the observed Rydberg transitions in allene if we assume that some of the observed bands are

TABLE VII. Rydberg series for allene.[a]

Rydberg orbital	Calculated term values	Experimental term values
$3sa_1$	3.07[b]	3.02[c]
$4s$	1.40	1.62
$5s$	0.80	0.88
$6s$	0.51	0.56
$3pb_2$	2.23[d]	2.17[e]
$4p$	1.10	1.25
$5p$	0.66	0.74
$6p$	0.44	0.49
$3pe$	2.24[f]	2.01[g]
$4p$	1.06	1.15
$5p$	0.56	0.69
$3d$	1.78[h]	1.83[i]
$4d$	1.02	1.02

[a]Ground state electronic configuration, $1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 3b_2^2 1e^4 2e^4 : {}^1A_1$.
[b]$\delta = 0.90$.
[c]$\tilde{B}\ ^1E$ state.
[d]$\delta = 0.53$.
[e]$\tilde{C}\ ^1E$ state.
[f]$\delta = 0.54$.
[g]$\tilde{D}\ ^1B_2$ state.
[h]$\delta = 0.23$.
[i]Average of term values for series V and VI.

vibrational members of a few basic series.

G. Butadiene

Rydberg states of butadiene appear in the absorption spectrum below 2000 Å. In the 2000–1600 Å there are strong single and double bands which probably represent single electronic transitions.[4] At shorter wavelengths Price and Walsh[25] have assigned two Rydberg series with quantum defects of 0.10 and 0.50 converging to an ion at 9.1 eV. Sugden and Walsh[26] observed another series with a quantum defect of 0.10 converging to an ion at 8.8 eV which they attribute to *cis*-butadiene.

Table VIII shows our assignments for the observed Rydberg series in *trans*-butadiene. The series with a quantum defect of 0.50 is assigned as an npb_u series. The other series with $\delta = 0.10$ cannot be either an nsa_g series with calculated term values of 2.71, 1.33, and 0.77 eV or an np series. We have assigned this as an nd series in which the molecule is distorted from C_{2h} symmetry in the upper state. We can also assign some of the bands in the 2000–1600 Å region, e.g., the $\tilde{E}\,^1A_u$ state, as early members of these Rydberg series.

H. Butene

Both *trans*- and *cis*-butene have similar spectra which resemble the spectrum of ethylene. All three spectra show a broad $N \leftarrow V$ absorption beginning at about 2600 Å in ethylene and at about 2100 Å in *trans*- and *cis*-butene. Slightly to the red side of this absorption both *cis*- and *trans*-butene show another absorption referred to as the mystery band. McDiarmid[27] has arranged the mystery and other bands of *trans*-butene into two Rydberg series with quantum defects of 0.88 and 0.24 converging to an ion at 9.2 eV. She[27] has also shown that the mystery band and other transitions in *cis*-butene can be arranged into another series with a quantum defect of 1.03 converging to an ion at 9.1 eV.

TABLE VIII. Rydberg levels for butadiene.[a]

Rydberg orbital	Calculated term values[b]	Experimental term values
$3pb_u$	2.01[c]	2.01[d]
$4p$	1.08	1.06[e]
$5p$	0.65	0.68[f]
$6p$	0.43	0.45
$3pa_u$	2.12[g]	2.25[h]
$4p$	1.09	···
$3d$	1.76[i]	1.61
$4d$	0.99	0.90[j]
$5d$	0.63	0.56

[a]Ground state electron configuration of *trans*-butadiene, $1a_g^2 1b_u^2 2b_u^2 2a_g^2 3a_g^2 3b_u^2 4a_g^2 4b_u^2 5a_g^2 5b_u^2 6a_g^2 6a_u^2 7a_g^2 1a_u^2$: ^1A_g.
[b]All term values in electron volts.
[c]Quantum defect $\delta = 0.40$.
[d]Average of the term values of the $E\,^1A_u$ and $\tilde{F}\,^1A_u$ states.
[e]$\tilde{G}\,^1A_u$ state.
[f]^1A_u series with series limit at 73 066 cm^{-1}.
[g]$\delta = 0.47$.
[h]$\tilde{D}\,^1B_u$ state.
[i]$\delta = 0.22$.
[j]Rydberg series will series limit at 73 115 cm^{-1}.

TABLE IX. Rydberg levels for butene.

Rydberg orbitals	Calculated term values[a]	Experimental term values
Trans		
$3s$	2.99[b]	3.04[c]
$4s$	1.39	1.36
$5s$	0.80	0.84
$6s$	0.50	0.55
$3da_g$	1.87[d]	1.76[e]
$4d$	0.96	1.00
$5d$	0.60	0.63
$6d$	0.44	0.44
Cis		
$3s$	2.97[f]	3.13[g]
$4s$	1.36	1.56
$5s$	0.78	0.85
$6s$	0.50	0.56

[a]All term values in electron volts.
[b]Quantum defect $\delta = 0.87$.
[c]^1A_u series will limit at 73 900 cm^{-1}.
[d]$\delta = 0.31$.
[e]^1A_u series with limit at 74 000 cm^{-1}.
[f]$\delta = 0.86$.
[g]$^1B_1$ series with a limit at 73 550 cm^{-1}.

The results of our model calculations in Table IX confirm these Rydberg series[25] and show the two series containing the mystery bands to be ns series. The other Rydberg series in *trans*-butene is an $nd\sigma$ series.

III. CONCLUSIONS

The main purpose of this paper has been to apply the simple model potential method developed in an earlier paper[1] to study the Rydberg series in a large number of polyatomic molecules. In this scheme the effective potential of the molecular core is represented by a sum of atomic model potentials calibrated to atomic data. With the results of these model calculations we have been able to assign and interpret almost all of the Rydberg series in the molecules we studied. We also assigned a number of previously unaccounted for progressions as transitions to Rydberg states and sometimes as complete series. We were also able to use the calculated term value for the $3p\sigma_u$ orbital to derive an estimate of 9.73 eV for the first ionization potential of nitrogen dioxide. Estimating this quantity has been difficult in most spectroscopic methods because of the large differences in nuclear geometry of the ground state and the various ions. By comparing calculated term values with the observed values our results allow us to identify Rydberg series which are perturbed by interloping valence transitions, e.g., in CO_2 and H_2CO.

The various applications discussed in these examples illustrate the utility of the model potential method for studying polyatomic molecules. Neither the calculated nor observed spectroscopic data need be of high ac-

curacy in order to carry out the analysis and assignments we have made in this paper. Finally the availability of quantum defects for many members of a Rydberg series can be useful in deriving phase shifts for studying scattering phenomena in polyatomic molecules such as CO_2 and H_2CO.

*Present address: Aerojet Electrosystems Co., Aerojet-General Corp., 1100 West Hollyvale, Azusa, CA 91702.
†Contribution No. 4661.

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